

鄂西香茶菜中一个新的苯取代二酮^{*}

赵 勇^{1,2,3}, 黄胜雄¹, 杨黎彬^{1,3}, 李丽梅¹,
肖伟烈¹, 普建新¹, 孙汉董^{1**}

(1 中国科学院昆明植物研究所植物化学与西部植物资源持续利用国家重点实验室, 云南 昆明 650204;

2 云南师范大学化学化工学院, 云南 昆明 650092; 3 中国科学院研究生院, 北京 100049)

摘要: 从青海产鄂西香茶菜 (*Isodon henryi*) 的叶中分离得到 1 个新的苯取代二酮, 利用波谱技术鉴定其结构。同时, 还得到了 8 个已知化合物。

关键词: 唇形科; 鄂西香茶菜; 苯基二酮

中图分类号: Q 946

文献标识码: A

文章编号: 0253-2700 (2008) 02-243-03

A New Phenylidione from *Isodon henryi* (Labiatae)

ZHAO Yong^{1,2,3}, HUANG Sheng-Xiong¹, YANG Li-Bin^{1,3}, LI Li-Mei¹,
XIAO Wei-Lie¹, PU Jian-Xin¹, SUN Han-Dong^{1**}

(1 State Key Laboratory of Phytochemistry and Plant Resources in West China, Kunming Institute of Botany, Chinese Academy of Sciences, Kunming 650204, China; 2 College of Chemistry and Engineering, Yunnan Normal University, Kunming 650092, China;

3 Graduate University of Chinese Academy of Sciences, Beijing 100049, China)

Abstract: A new phenylidione named henrydione (**1**), together with eight known compounds (**2** - **9**) were isolated from the ethyl acetate extract of *Isodon henryi*. The structure was elucidated on the basis of extensive NMR and MS means.

Key words: Labiatae; *Isodon henryi*; Phenylidione

In past studies, a variety of structurally interesting diterpenoids with various biological activities, such as antibacterial, anti-inflammatory and anticancer activities (Sun *et al.*, 2001), were discovered from medicinal plants of the genus *Isodon* (Labiatae). In our continuing efforts to discover more novel naturally bioactive diterpenoids, we investigated the acetone extract of the leaves of *Isodon henryi* collected from Qinghai province, and isolated a series of ent-kaurane diterpenoids (Zhao *et al.*, 2007). Besides, a new phenylidione, named henrydione, together with eight known compounds (**2** - **9**), cirsiol (2) (Linuma *et al.*, 1980),

oleanolic acid (**3**) (Tunmann and Baversfeld, 1975), ursolic acid (**4**) (Brieskom and Eberhardt, 1953), asiatic acid (**5**) (Zhang *et al.*, 1997), 5-hydroxy-7-methoxychromone (**6**) (Vasconcelos *et al.*, 1998), 10-undecenoic acid (**7**) (Sharma *et al.*, 1995), rosmarinic acid (**8**) (Eicher *et al.*, 1996) and methyl rosmarinate (**9**) (Lee *et al.*, 1992) were obtained. Henrydione, as a new natural occurring product, was the first isolation in the genus of *Isodon*. Here, we reported the isolation and elucidation of this new compound.

Henrydione (**1**), obtained as an amorphous solid,

* Foundation item: This study was financially supported by the Natural Science Foundation of Yunnan Province (2004C0008Z)

** Author for correspondence; Tel: +86-871-5223251; E-mail: hdsun@mail.kib.ac.cn

Received date: 2007-08-21, Accepted date: 2007-11-29

作者简介: 赵勇 (1967-) 男, 在读博士研究生, 主要从事天然产物化学研究。

has the molecular formula $C_{11}H_{12}O_5$ from HRESIMS (m/z : 247.0589 $[M+Na]^+$, calcd .247.0582). IR absorptions at 3430, 1711 cm^{-1} indicated the presence of hydroxyl and carbonyl groups, respectively. The ^{13}C NMR spectrum of **1** (Table 1) along with analysis of the DEPT spectra displayed 11 carbon signals corresponding to one methyl, one methylene, one oxygenated methine (δ 70.1), two carbonyl carbons (δ 206.4, 199.0) and six phenyl carbons. The typical signals at δ 7.91 (1H, d, $J=8.2$ Hz), δ 7.24 (1H, d, $J=8.2$ Hz) and δ 8.21 (1H, br s) observed in the 1H NMR spectrum revealed the presence of 1, 2, 4-trisubstituted phenolic moiety, which was also supported by the HMBC correlations from H - 2 (δ 8.21) to C - 3 (δ 147.5), C - 4 (δ 150.2) and C - 6 (δ 123.8), from H - 5 (δ 7.24) to C - 1 (δ 126.9), C - 3 (δ 147.5) and C - 4 (δ 150.2), and from H - 2 (δ 8.21) to C - 6 (δ 123.8). The side-chain of phenolic cycle was established by the HMBC correlations from H - 2 (δ 5.94) and H - 3 (δ 3.04, 3.22) to C - 1 (δ 199.0), from H - 2 (δ 5.94), H - 3 (δ 3.04, 3.22) and H - 5 (δ 2.16) to C - 4 (δ 206.4). The cross-peaks of H - 2 (δ 8.21) and H - 6 (δ 7.91) with C - 1 (δ 199.0) (Fig. 1) helped in assigning the attachment of the side-chain to be at C - 1. Thus, compound **1** was determined as 1-(3, 4-dihydroxyphenyl)-2-hydroxypentane-1, 4-dione.

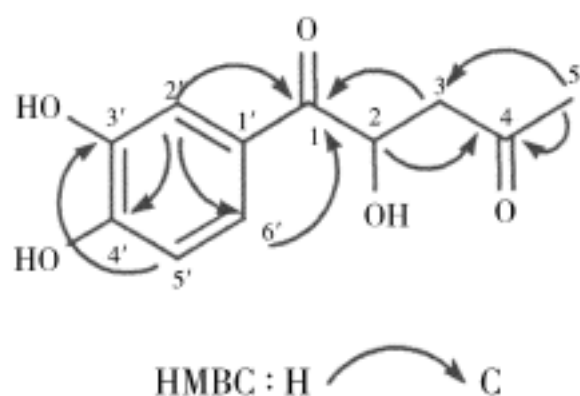


Fig. 1 Key HMBC correlations for **1**

The known compounds (**2** - **9**) were identified to be cirsiol (**2**), oleanolic acid (**3**), ursolic acid (**4**), asiatic acid (**5**), 5-hydroxy-7-methoxychromone (**6**), 10-undecenoic acid (**7**), rosmarinic acid (**8**) and methyl rosmarinate (**9**) by comparison of their spectral data with literature values.

Table 1 1H and ^{13}C NMR spectral data of compound **1** in C_5D_5N (1H : 400 MHz; ^{13}C : 100 MHz; δ : ppm)

No.	1	
	C	H
1	199.0 (s)	
2	70.1 (d)	5.94 (dd, 4.5, 7.9)
3	49.0 (t)	3.04 (dd, 8.0, 16.1) 3.22 (dd, 4.4, 16.1)
4	206.4 (s)	
5	30.7 (q)	2.16 (s)
6	126.9 (s)	
7	116.9 (d)	8.21 (br s)
8	147.5 (s)	
9	150.2 (s)	
10	116.2 (d)	7.24 (d, 8.2)
11	123.8 (d)	7.91 (br d, 8.2)

Experimental

General Experimental Procedures Optical rotations were measured using a Perkin-Elmer model 241 polarimeter. IR was recorded on a Bio-Rad FTS-135 spectrometer with KBr pellets. MS were obtained on a VG Auto spec-3000 spectrometer or on a Finnigan MAT 90 instrument. 1D and 2D NMR spectra were measured on Bruker AM-400 and Bruker DRX-500 instrument with TMS as internal standard, respectively. The EtOAc layer was decolorized on MCI-gel CHP 20P. Column chromatograph were performed either on silica gel (200 - 300 mesh, Qingdao Marine Chemical Inc., China), Lichroprep RP-18 gel (40 - 63 μm , Merck, Darmstadt, Germany) and Sephadex-LH-20 (25 - 100 μm , Amersham Biosciences, Sweden). Thin-layer chromatograph (TLC) was carried out on silica gel 60 F₂₅₄ on glass plates (Merck) using various solvent systems.

Plant Material The leaves of *I. henryi* were collected in Minhe County, Qinghai province, People's Republic of China, in July 2005 and identified by Prof. LI Xi-Wen, and a voucher specimens (KIB 200507014) has been deposited in the State Key Laboratory of Phytochemistry and Plant Resources in West China, Kunming Institute of Botany, Chinese Academy of Sciences.

Extraction and Purification The milled plant material (3.5 kg) was extracted with 70% aq. acetone (3×20 L) at r.t. overnight. The extract was partitioned between H_2O and EtOAc. The EtOAc layer (81 g) was chromatographed on MCI-gel CHP 20P (eluted with 90% CH_3OH-H_2O , then 100% CH_3OH). The 90% CH_3OH fraction (58 g) was chromatographed over silica gel (200 - 300 mesh), eluted in a step gradient manner with $CH_2Cl_2-Me_2CO$ (1:0 to 0:1) to afford seven fractions (A-G). Fraction B (4.53 g) was isolated by silica gel column chromatography [200 - 300 mesh, petroleum-acetone (9

1 - 1 1)] to give three isolates **3** (32 mg), **4** (4 mg) and **5** (17 mg). Fractions C (3.60 g) was chromatographed over silica gel (200 - 300 mesh) and divided into eight subfractions (**1** - **8**). Compound **1** (8 mg) was obtained by RP-18 (eluted with 42% CH₃OH) from fraction C - 2 (173 mg). Compound **2** (20 mg) and **6** (17 mg) was purified by Sephadex-LH-20 from fractions C - 3 (1.14 g). Fraction D (2.3 g) was further purified by silica gel column chromatography [200 - 300 mesh, eluted with petroleum-acetone (3 : 1)] to give compound **8** (5 mg) and compound **9** (5 mg). Fraction E (2.6 g) afforded compound **7** (7 mg) by silica gel column chromatography [200 - 300 mesh, eluted with petroleum-acetone (3 : 1)] and RP-18 (eluted with 30% CH₃OH) successively.

2-hydroxy-1-(3, 4-dihydroxyphenyl)-pentane-1, 4-dione (**1**): an amorphous solid; $[\alpha]_D^{25} + 145.7$ (c 0.1, C₅H₅N); IR_{max}^{KBr} cm⁻¹: 3430, 2923, 1711, 1612; ESIMS m/z : 247 [M + Na]⁺ (100), 471 [2M + Na]⁺ (6); HRESIMS m/z : 247.0589 (calcd. for C₁₁H₁₂O₅Na 247.0582); ¹H NMR (C₅D₅N, 400 MHz) and ¹³C NMR (C₅D₅N, 100 MHz) data see Table 1.

Acknowledgements: The authors are grateful to the Analytical Group, Laboratory of Phytochemistry, Kunming Institute of Botany, CAS for the spectral measurements.

References:

- Brieskom CH, Eberhardt KH, 1953. The oxytriterpane acid of *Salvia* [J]. *Arch Pharm*, **286**: 124—129
- Eicher T, Ott M, Speicher A, 1996. New synthesis of (+)-rosmarinic acid and related compounds [J]. *Synthesis*, **6**: 755—762
- Lee SM, Lai JS, Kuo YH, 1992. A new dilignol, methyl rosmarinate from the whole herb of *Elinopodium laxiflorum* [J]. *Chemistry Express*, **7**: 897—900
- Linuma M, Matsuura S, Kusuda K, 1980. Carbon-13 spectral of flavones [J]. *Chem Pharm Bull*, **28**: 708—716
- Sharma PK, Srivastava SK, Sharma S, 1995. A new synthesis of (4R, 5S)-2, 2-dimethyl-5-[(Z)-2-pentenyl]-1, 3-dioxolane-4-carboxaldehyde [J]. *Synthetic Communications*, **25**: 1249—1253
- Sun HD (孙汉董), Xu YL (许云龙), Jiang B (姜北), 2001. Diterpenoids from *Isodon* Species [M]. Beijing: Science Press
- Tunmann P, Bauersfeld HJ, 1975. Further components from radix *Harpagophytum procumbens* DC [J]. *Archiv der Pharmazia*, **308**: 655—657
- Vasconcelos J, Silva M, Cavaleiro J, 1998. Chromones and flavanones from *Artemisia campestris* subsp. *maritima* [J]. *Phytochemistry*, **49**: 1421—1424
- Zhao Y (赵勇), Huang SX (黄胜雄), Sun HD (孙汉董) *et al.*, 2007. Cytotoxic *ent*-kaurane Diterpenoids from *Isodon henryi* [J]. *Planta Medica* (submitted, PLAMED-2007-08-0603-0P)
- Zhang GL (张国林), Zhou ZZ (周正质), Li BG (李伯刚), 1997. Chemical investigation of *Morina chinensis* [J]. *Nat Prod Res Dev* (天然产物研究与开发), **9**: 10—13